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A Seismic Equation of State*

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Summary

Birch's hypothesis of a close relationship between seismic velocity and density is extended and modified so as to be in accord with theoretical predictions concerning the form of the equation of state. Although developed as a simple method to assure consistency between the seismic velocities and densities in free oscillation calculations the resulting equation of state is of quite general utility in geophysical studies where the seismic velocities, rather than hydrostatic pressure and temperature, are the directly measured variables. A simplified form of the seismic equation of state is

$$\rho = A\bar{M}\Phi^n$$

where ρ is the density, $\bar{M}$ is the mean atomic weight, n is a constant of the order of $\frac{1}{4}$ to $\frac{1}{3}$ and is related to the Grüneisen constant γ, and Φ is the seismic parameter $V_P^2 - (\frac{4}{3})V_S^2$. The exponent n is slightly different for constant temperature and constant pressure experiments but its magnitude, in both cases, can be estimated from lattice dynamics. On the other hand n is roughly the same number for compositional, structural and pressure effects.

Since Φ also is $(\partial P/\partial\rho)_S$ and K_S/ρ, data from static compression and shock wave as well as ultrasonic experiments can be used to determine the parameters in the equation of state and to extend its range beyond that available from ultrasonic data. Static pressure and shock wave data extend to much higher pressures, or compressions, than the ultrasonic data used by Birch and many more materials have been tested.

The general tendency of density to increase with Φ can be used to determine the density in the C-region even if this is a region of phase changes. New density models for the Earth are constructed on these considerations.

Notation and basic relationships

V = specific volume
$V_0 = V$ at $P = 0$
ρ = density $= \bar{M}/V$
$\rho_0 = \rho$ at $P = 0$
T = absolute temperature
P = pressure
S = entropy

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$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P = \text{volume thermal expansion} \tag{1A}$$

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \rho\left(\frac{\partial P}{\partial \rho}\right)_T = \text{isothermal bulk modulus} \tag{2A}$$

$$K_S = -V\left(\frac{\partial P}{\partial V}\right)_S = \rho\left(\frac{\partial P}{\partial \rho}\right)_S = \text{adiabatic bulk modulus} \tag{3A}$$

$$\Phi_S = K_S/\rho = V_P{}^2 - \tfrac{4}{3}V_S{}^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = \text{elastic ratio} \tag{4A}$$

$$\gamma = \alpha K_T/\rho C_V = \alpha K_S/\rho C_P = \text{Grüneisen's ratio} \tag{5A}$$

C_V = specific heat at constant volume

C_P = specific heat at constant pressure

V_P, V_S = velocity of compressional and shear waves

$$K_S = K_T(1+\alpha\gamma T) \tag{6A}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = K_T\alpha \tag{7A}$$

$$\left(\frac{1}{K_T}\right)\left(\frac{\partial K_T}{\partial T}\right)_P = -V\left(\frac{\partial \alpha}{\partial V}\right)_T \tag{8A}$$

$$\left(\frac{1}{K_T}\right)\left(\frac{\partial K_T}{\partial T}\right)_P = K_T\left(\frac{\partial \alpha}{\partial P}\right)_T \tag{9A}$$

θ = characteristic temperature (10A)

$\bar{M}$ = mean atomic weight

Bulk modulus = incompressibility = 1/compressibility.

1. Introduction

The power and the limitations of the classical Adams–Williamson method for determining the density structure of the Earth are well known. The method requires assumptions regarding the hydrostaticity, homogeneity and thermal state of the Earth. The major sources of error in the application of the method are the dominant effects of temperature in the upper mantle and the marked inhomogeneity of the *C*-region of the mantle between about 300 and 800 km in depth. This part of the Earth (the *C*-region) accounts for approximately 25% of the mass and 40% of the total moment of inertia, but it must be handled outside the framework of the Adams–Williamson method and a resulting density model is only plausible to the extent that the treatment of the *C*-region is plausible. All attempts to integrate through this region have been admittedly arbitrary. The same limitation is involved in the use of a theoretical equation of state, relating density and pressure, which is integrated with the help of the hydrostatic assumption.

The Earth consists of five major regions; the upper mantle, the transition or *C*-region, the lower mantle, the outer core and the inner core. In addition, both the lower mantle and the inner core have a transition region. Since the mass and the moment of inertia have been the only constraints on density models the problem is clearly under-determined.

Recent work indicates that there are two relatively sharp discontinuities in the upper mantle; one between 350–450 km and one between 600–700 km. These are almost certainly due to solid–solid phase changes but their presence further complicates the problem. The presence of the low-velocity zone in the upper mantle argues for a temperature or compositional effect that dominates the effect of self-compression in this region. The need for a different approach for obtaining the density structure of the Earth from seismic data is clearly indicated.

The primary motivation for this paper, however, is the new data that has become available that is pertinent to the density structure of the Earth, namely, the periods of free oscillation. The periods of free oscillation depend on the seismic velocities *and* the density and it is this data that has reopened the density question. Our basic postulate will be that the seismic velocities are primarily a function of molar volume and that the density variation in the Earth will tend to mimic the velocity changes. The constants relating density and seismic velocities can be adjusted in the various regions of the Earth in order to satisfy the mass, moment of inertia and free oscillation data.

The details and results of this method of finding the density structure of the Earth will appear in a later paper. The present paper develops the form of the relationship which is expected to hold between density and seismic velocities.

2. Birch's hypothesis

Birch (1961) discovered an important empirical relationship between compressional velocity, V_P, and density, ρ, which he put in the form

$$\rho = A(\bar{M}) + BV_P. \tag{1}$$

The constants were found experimentally from compressional velocity measurements on rocks and minerals of different structure and composition. The constant A was found to be, roughly, a function only of the mean atomic weight, $\bar{M}$. Birch postulated that this velocity–density relationship also held when the density change was due to compression rather than structure or composition. The necessary data to test this conjecture were not available but the hypothesis yielded reasonable density models for the mantle. One of the important features of density models using this relationship is the more gradual increase of density with respect to the compressional velocity in the lower mantle than given by the standard Adams–Williamson method. The density at the base of the mantle is some 0·40 g/cm^3 less than given by the Bullen model A. Furthermore, the constant A determined for the mantle from constraints supplied by the total mass and moment of inertia leads to an estimate of the mean atomic weight, i.e. a measure of the composition of the mantle.

The relationship provides a particularly useful method for handling the troublesome inhomogeneous C-region of the upper mantle if it is assumed that it holds through a phase change.

In a later paper Birch (1964) utilized this relationship to integrate through the low-velocity and transition regions but adopted the Adams–Williamson method for the lower mantle where he felt its use was most justified. In this way he did not have to assume that the empirical rule held outside its range of direct experimental verification.

The idea, however, of an intimate relationship between seismic velocity and density has much merit both on theoretical grounds and from practical considerations. We wish to exhume Birch's basic method in a slightly different form which allows us to extend its range of experimental verification and provide it with a theoretical basis.

Theoretical and experimental equations of state provide relationships between density, pressure and temperature. It would be extremely important to geophysics if the independent variables, temperature and pressure, which are unknown in the

Earth, could be replaced by seismic parameters which are well known. This would be the case if it could be demonstrated that some function of the seismic velocities depended mainly on volume, or density, and that temperature and pressure affected the seismic velocities only to the extent that the density was changed. Birch's hypothesis is one form of this idea.

The basic idea of this paper can be illustrated very quickly. Consider an equation of state of the form

$$P = (N-M)^{-1} K_0 \left[\left(\frac{\rho}{\rho_0}\right)^N - \left(\frac{\rho}{\rho_0}\right)^M \right], \tag{1}$$

where P = pressure, K_0 = initial bulk modulus, ρ_0 = initial density and ρ is the density at pressure P. Gilvarry (1957) has shown that a variety of theoretical considerations lead to an equation of this form; in particular $N = 7/3$, $M = 5/3$ gives the Birch–Murnaghan finite strain equation of state.

The conventional approach would invoke an equation of this type, along with an assumption of hydrostaticity, to integrate through a homogeneous self-compressed shell. Estimates of the temperature gradient and the coefficient of thermal expansion would be used to make a temperature correction. K_0 and ρ_0 are functions of the initial conditions, i.e. composition and temperature. These initial conditions would have to be reset at the top of each of the various regions of the Earth. The derivative of (1) with respect to density gives

$$\frac{\partial P}{\partial \rho} = (N-M)^{-1} \frac{K_0}{\rho_0} \left[N\left(\frac{\rho}{\rho_0}\right)^{N-1} - M\left(\frac{\rho}{\rho_0}\right)^{M-1} \right], \tag{2}$$

or

$$\Phi = \Phi_0 (N-M)^{-1} \left[N\left(\frac{\rho}{\rho_0}\right)^{N-1} - M\left(\frac{\rho}{\rho_0}\right)^{M-1} \right], \tag{3}$$

where Φ is the ratio of the bulk modulus to the density. The adiabatic Φ for the Earth is available from seismic data.

The ratio of Φ for two different densities is then

$$\frac{\Phi_1}{\Phi_2} = \frac{N(\rho_1/\rho_0)^{N-1} - M(\rho_1/\rho_0)^{M-1}}{N(\rho_2/\rho_0)^{N-1} - M(\rho_2/\rho_0)^{M-1}}. \tag{4}$$

If the total compression is small

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right) = N + M - 1, \tag{5}$$

or

$$\frac{\rho_2}{\rho_1} = \left(\frac{\Phi_2}{\Phi_1}\right)^{1/(N+M-1)}. \tag{6}$$

Equation (6) gives densities 0·5% lower at 10% compression ($\Delta\rho/\rho$) and 1·7% lower at 20% compression than equation (4) for the Birch exponents. Equation (5) can be considered an approximation to equation (4) but it is a perfectly good equation of state in its own right and follows immediately from Murnaghan's 'integrated linear theory of finite strain' as we shall show later. It implies that the bulk modulus is a linear function of pressure, a quite common assumption and observation.

Now, given the initial conditions Φ_1 and ρ_1 we can determine ρ_2 from Φ_2 by equations (4) or (6) just as the initial conditions ρ_0, K_0 and $P(0)$ determine ρ when P is given by a standard equation of state such as (1). Under certain conditions the gradient of Φ with depth yields immediately the gradient of density with depth.

We now have the embryo of a 'seismic equation of state' that deals, potentially, with measured seismic parameters in the place of pressure.

In practice, of course, we must contend with adiabatic, instead of isothermal, constants and we must consider effects other than pressure controlling the relationship between seismic properties and density. It will be shown, however, that an equation of the form of (6) has quite general utility.

In the following sections we will investigate the effect of pressure, composition, phase and temperature on this relation and derive the necessary isothermal–adiabatic transformations.

3. Isothermal–adiabatic transformations

Seismic data is adiabatic in the sense that the time scale of seismic waves is short compared to the time scale required for the temperature to equilibrate between the compressed and dilated parts of the wave. Most of the theory and much of the laboratory data pertinent to the behaviour of solids under high pressure is for isothermal conditions. To relate the isothermal theories and experiments with the adiabatic seismic data requires isothermal–adiabatic transformations all of which follow from

$$K_S = K_T(1+\alpha\gamma T). \tag{6A}$$

A large amount of ultrasonic data on solids at moderate pressures has accumulated in the last decade and these transformations are also required to interpret this data in terms of isothermal equations of state.

From (6A) we can write immediately

$$\frac{(\partial \ln K_S/\partial T)_P}{(\partial \ln\rho/\partial T)_P} = \frac{(\partial \ln K_T/\partial T)_P}{(\partial \ln\rho/\partial T)_P} - \frac{K_T}{\alpha K_S}\left(\frac{\partial \alpha\gamma T}{\partial T}\right)_P, \tag{7}$$

$$\frac{(\partial \ln K_S/\partial P)_T}{(\partial \ln\rho/\partial P)_T} = \frac{(\partial \ln K_T/\partial P)_T}{(\partial \ln\rho/\partial P)_T} + \frac{\alpha\gamma T K_T}{K_S}\left[\left(\frac{\partial \ln\gamma}{\partial \ln\rho}\right)_T - \left(\frac{\partial \ln K_T}{\partial \ln\rho}\right)_P\right]. \tag{8}$$

The Grüneisen ratio, γ, is relatively independent of temperature and the coefficient of volume thermal expansion is independent of temperature at high temperatures. The second term on the right of equation (7) is, therefore, of the order of γ and is negative. The volume dependence of γ can be written:

$$\left(\frac{\partial \ln\gamma}{\partial \ln V}\right)_T = \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P + 1 = -\frac{1}{\alpha}\left(\frac{\partial \ln K_T}{\partial T}\right)_V + 1, \tag{9}$$

if we take $(\partial \ln C_V/\partial \ln V)_T = 0$, appropriate for high temperatures. Note that the multiplicative factor $\alpha\gamma TK_T/K_S$ in equation (8) can be written $(K_S - K_T)/K_S$ which is a small number of the order of 0·01 for most materials at room temperature. The derivative $(\partial \ln\gamma/\partial \ln\rho)_T$ is of the order of minus one and $(\partial \ln K_T/\partial \ln\rho)_P$ is of the order of six so the second term on the right-hand side of equation (8) is of the order of $-0{\cdot}07$ or about 1% of the first term.

These considerations have been further developed by Overton (1962), Swenson (1964), Anderson (1966) and Thurston (1965). These authors have computed the isothermal–adiabatic transformations for some elements and compounds neglecting only the temperature dependence of the Grüneisen ratio. Table 1 has been computed from their data.

The notation is:

$$\frac{(\partial \ln K_T/\partial P)_T}{(\partial \ln\rho/\partial P)_T} = \left(\frac{\partial \ln K_T}{\partial \ln\rho}\right)_T = \left(\frac{\rho\partial K_T}{K_T\partial\rho}\right)_T = \left(\frac{\partial K_T}{\partial P}\right)_T, \tag{10}$$

$$\frac{(\partial \ln K_S/\partial P)_T}{(\partial \ln\rho/\partial P)_T} = \left(\frac{\partial \ln K_S}{\partial \ln\rho}\right)_T = \left(\frac{\rho\partial K_S}{K_S\partial\rho}\right)_T = \frac{K_T}{K_S}\left(\frac{\partial K_S}{\partial P}\right)_T, \tag{11}$$

Table 1

Material	$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P$	$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_T$	$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P$	$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T$	$\left(\frac{\partial \ln K_T}{\partial T}\right)_V$ $\times 10^5$	$\left(\frac{\partial \ln K_S}{\partial T}\right)_V$ $\times 10^5$
Cu	5·69	5·62	3·23	5·43	— 0·28	+10·89
Ag	6·19	6·21	3·26	5·93	+ 0·17	+15·38
Au	7·03	6·50	3·92	6·20	— 2·24	+ 9·64
MgO (ceramic)	5·27	3·95	2·40	3·86	— 4·16	+ 4·60
MgO (single crystal)	5·66	4·54	2·54	4·35	— 3·53	+ 5·70
Al_2O_3	6·13	4·00	3·16	3·76	— 3·47	+ 0·81
α-quartz	6·44	6·34	5·34	6·28	— 0·36	+ 3·35
Mg	5·34	4·16	3·70	3·92	— 8·80	+ 1·67
Fe	3·25	5·06	0·85	5·04	+ 6·35	+14·71
Si	2·14	4·16	1·32	4·15	+14·12	+19·78

$$\frac{(\partial \ln K_T/\partial T)_P}{(\partial \ln \rho/\partial T)_P} = \left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P = \left(\frac{\rho \partial K_T}{K_T \partial \rho}\right)_P = (K_T \alpha)^{-1} \left(\frac{\partial K_T}{\partial T}\right)_P, \tag{12}$$

$$\frac{(\partial \ln K_S/\partial T)_P}{(\partial \ln \rho/\partial T)_P} = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P = \left(\frac{\rho \partial K_S}{K_S \partial \rho}\right)_P = (K_S \alpha)^{-1} \left(\frac{\partial K_S}{\partial T}\right)_P. \tag{13}$$

The elastic moduli of a solid are affected by temperature both implicitly, through the volume, and explicitly. Thus, for example,

$$K_T = K_T(V, T)$$

and

$$d \ln K_T = (\partial \ln K_T/\partial V)_T dV + (\partial \ln K_T/\partial T)_V dT. \tag{14}$$

The measured variation of K_T with temperature is, then,

$$\left.\begin{aligned} \frac{d \ln K_T}{dT} &= \left(\frac{\partial \ln K_T}{\partial V}\right)_T \frac{dV}{dT} + \left(\frac{\partial \ln K_T}{\partial T}\right)_V, \\ \left(\frac{d \ln K_T}{d \ln V}\right)_P &= \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T + \alpha^{-1} \left(\frac{\partial \ln K_T}{\partial T}\right)_V, \end{aligned}\right\} \tag{15}$$

where $(\partial \ln K_T/\partial T)_V$ is the intrinsic temperature dependence of K_T. This intrinsic temperature dependence is also given in Table 1 for both K_T and K_S. Note that $(\partial \ln K_T/\partial T)_V$ can be either positive or negative but $(\partial \ln K_S/\partial T)_V$ is invariably positive.

No safe generalization can be made about the relative magnitude of the intrinsic temperature dependence of K_S compared to K_T. It is sometimes assumed that the intrinsic effect of temperature is greater for the adiabatic than the isothermal bulk modulus but this is not borne out by Table 1. There is a general tendency, however, for $(\partial \ln K_T/\partial T)_V$ to be smaller for those materials which are tested at high T/θ. In any event, Table 1 shows the relative effects of temperature and pressure on the relationship between bulk modulus and volume and shows that

$$\left(\frac{\partial \ln K_S}{\partial \ln V}\right)_P < \left(\frac{\partial \ln K_S}{\partial \ln V}\right)_T,$$

$$\left(\frac{\partial \ln K_S}{\partial \ln V}\right)_P \ll \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P,$$

and

$$\left(\frac{\partial \ln K_S}{\partial \ln V}\right)_T < \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T,$$

all of which are useful when trying to estimate the effects of P, V and T on the adiabatic bulk modulus. Note that these are all experimental and thermodynamic inequalities and are independent of the equation of state.

The seismic parameter Φ is simply

$$\Phi = K_S/\rho$$

so that

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_P = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P - 1, \tag{16}$$

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_T = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T - 1. \tag{17}$$

Table 2 gives experimental values for some materials of geophysical interest. Shock wave data is not isothermal but it has been tabulated under $(\partial \ln \Phi/\partial \ln \rho)_T$ since the main effect is due to pressure. The values in Table 2 can be considered empirical determinations of the quantity $(N+M-1)$ of equation (5).

Table 2

	$(\partial \ln \Phi/\partial \ln \rho)_T$	$(\partial \ln \Phi/\partial \ln \rho)_P$
MgO (ceramic, 34·6 °C)	2·99	1·63
MgO (ceramic, −78·5 °C)	2·86	1·40
MgO (single crystal)	3·35	1·54
MgO (shock wave)	5·59	
Al_2O_3 (ceramic)	2·76	2·19
Al_2O_3 (ceramic)	3·14	2·79
Al_2O_3 (shock wave)	6·27	
Granite (shock wave)	2·11	
Albite (shock wave)	2·42	
Diabase (shock wave)	2·88	
Fayalite (shock wave)	2·48	
Pyrolucite (shock wave)	6·08	
Forsterite (shock wave)	3·27	

* Shock wave data is from McQueen & Marsh (unpublished) and represents a least square fit to raw Hugoniot data uncorrected for temperature. The remaining data is from Schreiber & Anderson (1966a, b) and Anderson (1966).

4. Effect of temperature

We have discussed the relative effect of temperature on the isothermal and adiabatic bulk moduli but have made no attempt to discuss the absolute effect of temperature on an isothermal equation of state. The details of an accurate treatment of this effect are cumbersome, even when gross simplifications are made. The details are unimportant here. We have in hand, experimentally, the basic data concerning the bulk modulus for many solids and we need only inquire as to how temperature will affect these data.

The pressure and the isothermal bulk modulus are volume derivatives, at constant temperature, of the Helmholtz free energy $A(V, T)$. The corresponding adiabatic quantities are volume derivatives of the internal energy $U(V, S)$, at constant entropy. The equation of state of simple solids subjected to hydrostatic pressure can be written in two alternative forms. The *vibrational* formulation splits the Helmholtz free energy of the solid into the *lattice* energy, $U_L(V)$, which is the energy of a static solid of volume

V in its electronic ground state and a *vibrational* energy $U^*(V, T)$. The *thermal* formulation splits the Helmholtz free energy into a non-thermal *cohesive* energy $U_C(V)$ of the solid of volume V at 0°K and a *thermal* energy $U^*(V, T)$. Note that the lattice and cohesive energies depend only on volume and the terms with asterisks depend, in general, on both volume and temperature; in the Hildebrand approximation the thermal and vibrational energies are taken to be a function of temperature alone, this being a good approximation at high temperatures where the heat capacity at constant volume has attained its classical value. (See, for example, Fumi & Tosi 1962.) The cohesive energy is the free energy required to assemble the atoms from infinity to form the rigid lattice. The $U_C(V)$ includes both static lattice and zero point energy contributions. The total vibrational energy of the solid is the sum over all the modes of lattice vibration of all the particles. The vibrational energy $U^*(V, T)$ consists of the zero-point vibrational energy, $U^*(V, 0)$, of the normal modes at $T = 0$°K plus the energy required to heat the lattice at constant volume, V, from 0°K to T°K, i.e.

$$U^*(V, T) = U^*(V, 0) + \int_0^T C_V \, dT. \tag{18}$$

The Helmholtz free energy, in the Hildebrand approximation, can be written, for example,

$$A(V, T) = U_C(V) + U^*(T) - TS(V, T). \tag{19}$$

Since

$$P = -(\partial A/\partial V)_T$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T,$$

we have

$$P(V, T) = -\frac{\partial U_C(V)}{\partial V} + \alpha K_T T = P(V) + P^*(V, T) \tag{20}$$

and

$$\left.\begin{aligned} K_T(V, T) &= V\left(\frac{\partial^2 U_C(V)}{\partial V^2}\right)_T - VT\left(\frac{\partial \alpha K_T}{\partial V}\right)_T \\ &= K_T(V) + K_T^*(V, T), \end{aligned}\right\} \tag{21}$$

or

$$K_T(V, T) = K_T(V, 0) + T\alpha K_T(V, T)\left[\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T\right],$$

or

$$K_T(V, T) = K_T(V, T_0) + (T - T_0)\alpha K_T\left[\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T\right].$$

The quantity

$$\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T$$

is of the order of -1 (see Fürth 1944, Table 1, and also Table 1 of this paper). The quantity αK_T is of the order of 10 to 100×10^{-3} kb/°K for elements and is between about 30 and 70×10^{-3} for compounds of interest in the deeper mantle.

$$\alpha K_T\left[\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T\right]$$

is of the order of -50×10^{-3} kb/°K and a temperature rise of some 2000° K changes the bulk modulus by about 100 kb, which is about 10% of estimated values for the bulk modulus in the mantle.

The pressure in the mantle rises to about 1500 kb which, for $(dK/dP)_T = 4$ corresponds to a 6000 kb increase in the bulk modulus. Temperature can therefore be treated as a small perturbation on the general trend of bulk modulus, or Φ, with depth, at least in the deeper part of the mantle.

The thermal pressure, P^*, can be viewed as the radiation pressure exerted on the solid by completely diffuse elastic waves, i.e.

$$P^* = \frac{U_p}{V}\left(\tfrac{1}{3} - \frac{V\partial V_p}{V_p \partial V}\right) + 2\frac{U_s}{V}\left(\tfrac{1}{3} - \frac{V}{V_s}\frac{\partial V_s}{\partial V}\right) = \frac{-U_p}{\theta_p}\frac{\partial \theta_p}{\partial V} - 2\frac{U_s}{\theta_s}\frac{\partial \theta_s}{\partial V},$$

where the U_m, V_m and θ_m are the thermal energies, elastic wave velocities and characteristic temperatures associated with the longitudinal (P) and transverse (S) waves, (Brillouin 1964). The characteristic temperatures, θ, are defined as

$$\theta_m = \frac{h}{k} V_m \left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}},$$

where h is Planck's constant, k is Boltzmann's constant and $3N$ is the total number of degrees of freedom. Introducing the Grüneisen ratios

$$\gamma_m = \frac{-d \ln \theta_m}{d \ln V},$$

and the high-temperature form for the internal energy

$$U_m = RT,$$

we have

$$P^* = + \frac{RT}{V}\gamma_p + 2\frac{RT}{V}\gamma_s$$

or, for $\gamma_p = \gamma_s$

$$P^* = \frac{3RT\gamma\rho}{M}.$$

The thermal pressure can be written in a form analogous to the perfect gas equation (Brillouin 1964).

$$P^* = \frac{Q}{V}RT, \qquad Q = \gamma_p + 2\gamma_s,$$

where Q is of the order of 5 or 6 for many elements and is near 4 for MgO and Al_2O_3.

5. The equation of state

The general form of an equation of state follows from considerations of elementary thermodynamics and solid state physics. Gilvarry (1957) has shown that a wide variety of theoretical considerations all lead to an isothermal equation of state that can be expressed as

$$P = 3K_0(m-n)^{-1}[(V_0/V)^{\frac{1}{3}(m+3)} - (V_0/V)^{\frac{1}{3}(n+3)}], \tag{22}$$

$$K_T = K_0(m-n)^{-1}[(m+3)(V_0/V)^{\frac{1}{3}(m+3)} - (n+3)(V_0/V)^{\frac{1}{3}(n+3)}]. \tag{23}$$

The choice of exponents $m = 2$, $n = 4$ leads to Birch's equation which is based on finite strain considerations; if $m = 1$, $n = 2$ we obtain Bardeen's equation which was derived from quantum mechanical considerations. If $m = -3$ we obtain Murnaghan's equation which is based on an 'integrated linear theory of finite strain'. A generalized form of the equation of state of a degenerate electron gas obeying Fermi–Dirac statistics

can also be cast into this form. Equations of state based on the Mie form of the potential energy $U(r)$ of an atom in a central interatomic force field, given as

$$U(r) = -Ar^{-m} + Br^{-n},$$

where the two terms on the right correspond to an attractive and a repulsive potential and r is an interatomic distance, yield the general form of the equation of state by differentiation. The choice $m = 1$ is appropriate for electrostatic interactions and $m = 6$, $n = 12$ is the Lennard–Jones potential.

The foundations of the atomic approach were laid near the beginning of this century by Born, Von Kármán, Grüneisen, Madelung, Mie and Debye. The basic premise of the theory is that ionic crystals are made up of positively charged metal atom ions and negatively charged electronegative atom ions which interact with each other according to simple central force laws. The electrostatic, or coulomb, forces which tend to contract the crystal are balanced by repulsive forces which, in the classical theory, are of uncertain origin. Dipole–dipole and higher order interactions, the Van der Waals forces, provide additional coupling between ions. They dominate the attraction between closed-shell atoms but are a minor part of the total attractive force in mainly ionic crystals. The Van der Waals forces are also much shorter range than electrostatic forces.

The calculation of the exact form of the interatomic force law or the potential energy of an assembly of particles as a function of their separation is a very difficult problem and has been treated by quantum mechanical methods for only a few cases. For many purposes it is sufficient to adopt a fictitious force law which resembles the real one in some general features and which can be made to fit it in a narrow region around the equilibrium point. The total energy U must satisfy

$$\left(\frac{dU}{\partial V}\right)_{V_0} = 0 \quad \text{and} \quad \left(\frac{d^2U}{dV^2}\right)_{V_0} = \frac{K_T}{V_0}, \tag{24}$$

which are the conditions that the crystal be in equilibrium with all forces and that the theoretical bulk modulus, K_T, should be equal to the observed value. These conditions serve to determine the constants in the fictitious force law and assure that the slope and curvature of this law are proper at the equilibrium point.

The attractive forces in a crystal are balanced by the so-called overlap repulsive forces which oppose the interpenetration of the ions. Perhaps the simplest picture is a rigid ion surrounded by a free electron gas. The effect of hydrostatic pressure is to reduce the volume of the electron gas and to raise its kinetic energy. The kinetic energy varies as r^{-2} where r is the nearest neighbour separation. The repulsive force between ions is very small until the ions come in contact and then it increases more rapidly than the electrostatic force. In his early work on ionic crystals Born assumed that the repulsive forces between ions gave rise to an interaction energy of the type

$$U(r) = b/r^n,$$

for the whole crystal where b and n are constants and r is the distance between nearest unlike ions. Investigations of interionic forces based on quantum mechanics indicate that a repulsive potential of this type cannot be rigorously correct, although it may be a good approximation for a small range of r. Later work has used a repulsive potential of the form

$$U(r) = be^{-r/a},$$

where b and a are constants.

Regardless of the details of the various attractive and repulsive potentials and their dependence on interatomic spacing, the Mie–Lennard–Jones potential

$$U(r) = -Ar^{-m} + Br^{-n} \qquad n > m$$

is a simple useful approximation for a restricted region of the potential energy curve and, in particular, the vicinity of the potential minimum. A, B, m and n will be determined at a point in the vicinity of interest by requiring that the interatomic spacing and the bulk modulus both be appropriate for the pressure at this point.

Using the interatomic potential

$$U = -\frac{A}{r^m} + \frac{B}{r^n}, \qquad n > m \tag{25}$$

and setting the molar volume of the solid $V = \bar{M}/\rho$ equal to a constant times r^3 and using the relations

$$P = -\left(\frac{\partial U}{\partial V}\right)_T,$$

and

$$K_T = -\left(\frac{V\partial P}{\partial V}\right)_T,$$

for the pressure and bulk modulus respectively, we obtain

$$P = \frac{3K_0}{m-n}\left[\left(\frac{V_0}{V}\right)^{\frac{1}{3}(m+3)} - \left(\frac{V_0}{V}\right)^{\frac{1}{3}(n+3)}\right], \tag{26}$$

$$K = \frac{K_0}{m-n}\left[(m+3)\left(\frac{V_0}{V}\right)^{\frac{1}{3}(m+3)} - (n+3)\left(\frac{V_0}{V}\right)^{\frac{1}{3}(n+3)}\right], \tag{27}$$

where V_0 and K_0 are the molar volume and the bulk modulus at $P = 0$. These are the same as the general forms (22) and (23).

For small compressions we can expand K about $V = V_0$ to obtain

$$\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T = -\tfrac{1}{3}(m+n+6) \tag{28}$$

and can note in passing that

$$\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T = \left(\frac{\partial \ln K/\partial P}{\partial \ln V/\partial P}\right)_T = -\left(\frac{\partial K}{\partial P}\right)_T \tag{29}$$

so, to a first approximation, the isothermal bulk modulus is a linear function of pressure and a simple power law relationship holds between the bulk modulus and the density. Grüneisen (1912) and Fürth (1944) obtain $-\frac{1}{3}(m+n+9)$ for $(\partial \ln K/\partial \ln V)_T$ since they define the bulk modulus as $-V_0\partial P/\partial V$ instead of $-V\partial P/\partial V$ as above. We also note that $(\partial K/\partial P)_T$ is close to 4 for many substances giving $m+n = 6$ and since $n > m$ we have $5 < n < 6$.

The determination of

$$\left(\frac{\partial \ln K}{\partial \ln V}\right)_P = \frac{(\partial \ln K/\partial T)_P}{(\partial \ln V/\partial T)_P}$$

requires knowledge of the lattice sums but for $m = 3$

$$\left(\frac{\partial \ln K}{\partial \ln V}\right)_P = -\tfrac{1}{3}(m+n+3) = \left(\frac{\partial \ln K}{\partial \ln V}\right)_T + 1, \tag{30}$$

(Grüneisen 1912, Fürth 1944). Fürth tabulates this quantity for face-centred cubic lattices for a variety of m and n. His tabulation shows that

$$\left|\left(\frac{\partial \ln K}{\partial \ln V}\right)_P - \left(\frac{\partial \ln K}{\partial \ln V}\right)_T\right| \leqslant 1.$$

Using Grüneisen's approximation for $(\partial \ln K_T/\partial T)_P/(\partial \ln V/\partial T)_P$ we can summarize the important results of the previous sections.

For small compressions:

$$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_T = \tfrac{1}{3}(m+n+6),$$

$$\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P = \tfrac{1}{3}(m+n+9),$$

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T = \tfrac{1}{3}(m+n+6)+\frac{K_T{}^2}{K_S}\left(\frac{\partial \alpha\gamma T}{\partial P}\right)_T,$$

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P = \tfrac{1}{3}(m+n+9)-\frac{K_T}{\alpha K_S}\left(\frac{\partial \alpha\gamma T}{\partial T}\right)_P,$$

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_T = \tfrac{1}{3}(m+n+3)+\frac{K_T{}^2}{K_S}\left(\frac{\partial \alpha\gamma T}{\partial P}\right)_T,$$

$$\left(\frac{\partial \ln \Phi}{\partial \ln \rho}\right)_P = \tfrac{1}{3}(m+n+6)-\frac{K_T}{\alpha K_S}\left(\frac{\partial \alpha\gamma T}{\partial T}\right)_P,$$

or

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_T = \tfrac{1}{3}(m+n+6)-\frac{\alpha\gamma T K_T}{K_S}\left[\left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P-\left(\frac{\partial \ln \gamma}{\partial \ln \rho}\right)_T\right],$$

$$\left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P = \tfrac{1}{3}(m+n+9)-\frac{\gamma K_T}{K_S}+\frac{\alpha\gamma T K_T}{K_S}\left[\left(\frac{\partial \ln \gamma}{\partial \ln \rho}\right)_P+\left(\frac{\partial \ln \alpha}{\partial \ln \rho}\right)_P\right],$$

and corresponding equations for $(\partial \ln \Phi/\partial \ln \rho)$.

The Debye theory leads to a non-thermal definition of the Grüneisen ratio (Slater 1939, Lorentz 1916, Gilvarry 1956):

$$\gamma_D = -\tfrac{1}{6}-\tfrac{1}{2}\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T. \tag{31}$$

An alternative expression has been suggested by Druyvesteyn & Meyering (1941) and Dugdale & MacDonald (1953):

$$\gamma_{DM} = -\tfrac{1}{2}-\tfrac{1}{2}\left(\frac{\partial \ln K_T}{\partial \ln V}\right)_T = \gamma_D-\tfrac{1}{3}, \tag{32}$$

and this has been shown by Gilvarry (1956) to correspond physically to a model of independent pairs of nearest neighbour atoms rather than to the Debye model of coupled atomic vibrations. This definition of the Grüneisen ratio is often used in the reduction of shock wave data.

Further discussions of the Grüneisen parameter can be found in Barron (1957) and Fumi & Tosi (1962). These authors discuss the assumptions involved in equating the thermal and non-thermal definitions of the Grüneisen ratio. We can consider γ simply as a small parameter of the order of unity for present purposes.

Using these relations and equation (28) we can write

$$\gamma_D = \tfrac{1}{6}[m+n+5] \tag{33}$$

and

$$\gamma_{DM} = \tfrac{1}{6}[m+n+3], \tag{34}$$

which shows that the exponents in the equation of state are related to the anharmonic properties of the solid since the Grüneisen relation $\alpha = \alpha K_T/C_V$, relating the coefficient of thermal expansion, α, with the specific heat, C_V, is a measure of anharmonicity.

The parameter γ decreases with compression but has a tendency to be higher for the closer packed crystal structures such as face centred cubic and hexagonal close packing than it is for the more open structures such as diamond structure and body centred cubic. For most materials γ is between 1 and 2, which gives a range for $m+n$ of 1 to 7 for the Lorentz–Slater theory and 3 to 9 for the DM theory. The corresponding ranges for $(\partial \ln K_T/\partial \ln V)_T$ are 2·3 to 4·3 and 3 to 6 respectively, in agreement with Table 1.

6. Effect of composition and phase

We have now established the theoretical form for the expected relationship between Φ and density and have investigated the effect of temperature and pressure. The exponent in the power law relationship is different for temperature and pressure; i.e. there is an intrinsic temperature effect over and above the effect of temperature on volume. However, the effect of pressure, in general, dominates the effect of temperature.

We have not yet specifically allowed for composition except insofar as this information is contained in the initial density and Φ_0. Birch has shown empirically that the mean atomic weight, $\bar{M}$, is an appropriate measure of composition although exceptions to this general rule occur (Simmons 1964). Knopoff & Uffen (1954) have used

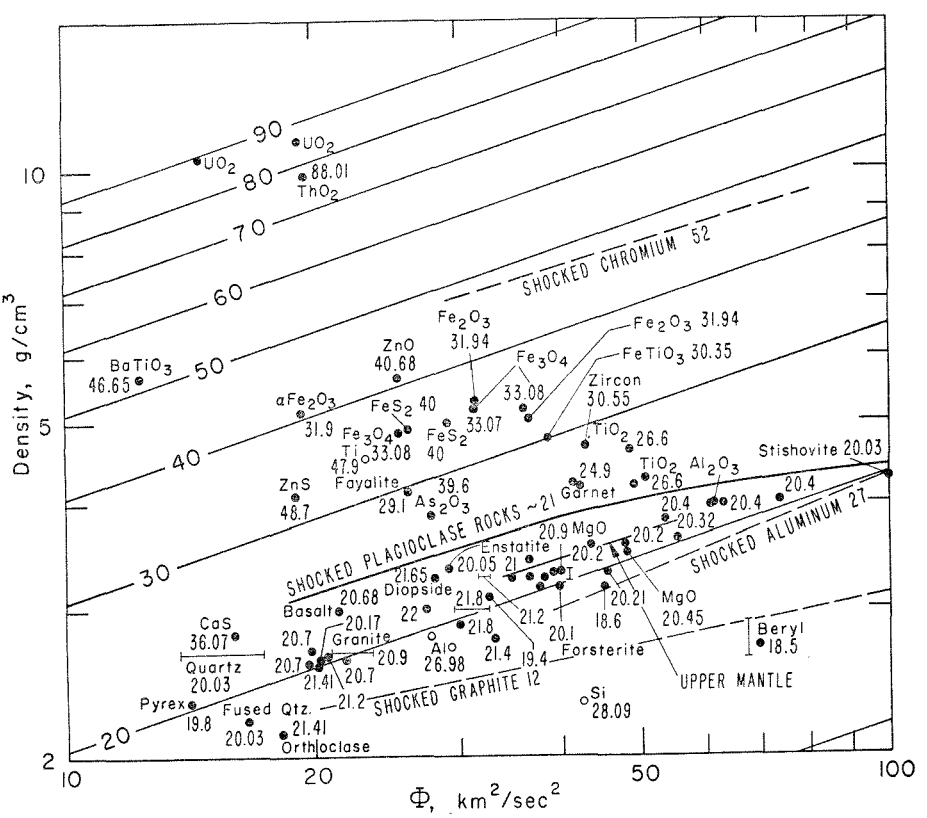

FIG. 1. Density vs Φ with mean atomic weight, $\bar{M}$, as the parameter for silicates, oxides, and some elements.

a 'representative atomic number' Z as a measure of composition in applying the Thomas–Fermi–Dirac (TFD) theory to compounds.

McMillan (1958) and Knopoff (1965) made semi-empirical adjustments to the Thomas–Fermi statistical model of the atom in order to obtain the proper low-pressure limit. Their equations can be put in the forms

$$-5(K_0 Z^{-10/3})(ZV_0)^{-1} = d(P_{TF} Z^{-10/3})/d(ZV)_{V=V_0}$$

and

$$(K_0 Z^{-10/3})(ZV_0)^{7/3} = \text{constant}.$$

The latter form (Knopoff 1965) can be written approximately as

$$\Phi_0 = \text{constant } (\rho_0/\bar{M})^{4/3}. \tag{35}$$

Although the Thomas–Fermi model is not appropriate for pressures as low as those existing in the Earth and the extrapolation to zero pressure conditions is not justified because of the presence of phase changes, equation (35) does suggest the form of the relationship between ϕ_0, ρ_0 and composition $\bar{M}$. At this stage the constants are more properly obtained from experiment.

Fig. 1 gives density, Φ and mean atomic weight for various oxides and silicates including natural rocks measured under moderate pressure in order to remove the effects of porosity. The quality of the data is variable and is probably most reliable for the synthetic oxides and single crystals. Most of the data is for adiabatic conditions; some is from isothermal compression experiments and some is from shock wave experiments. Most of the data for rocks is computed from the compressional velocity measured by Birch (1960) and the shear velocity measured by Simmons (1964), both at 10 kb; the density at 10 kb was not measured by these investigators so the 10 kb Φ was plotted against the zero pressure ρ. The data for rocks at 10 kb is not corrected for changes in dimension of the sample. The velocities are therefore too high by 1 or 2% and the density is too low by about 1%. The error in measuring velocity is about 1% and the spread of values for several samples from a given rock is about 1 or 2%. The systematic error in ρ and ϕ decreases with increasing ϕ because of the smaller dimension changes associated with the higher bulk modulus. Most of the oxides and minerals were measured at atmospheric pressure but there are a few points from shock wave experiments. There is also some isothermal data on the figure. In spite of the scatter and the varying quality of the data there is a clear relationship between ρ, Φ and $\bar{M}$. A least squares fit to this data yields

$$\frac{\rho}{\bar{M}} = 0{\cdot}0565\,\Phi^{0{\cdot}28} \tag{36}$$

with a standard deviation of 0·38 in density.

The mean atomic weight varies from 18·6 to 90·01 and the density varies from 2·21 to 10·36 g/cm^3 for the materials used in the least square fit. The range of mean atomic weight for materials of geophysical interest is much more restricted. For example, SiO_2, MgO, Al_2O_3, Fe_2O_3 and Fe_3O_4 all fall in the range 20 to 33.

Table 3 gives $\bar{M}$, ρ and Φ for thirty-one selected minerals and rocks which vary between 18·6 and 33·08 in mean atomic weight. This data is also plotted in Fig. 2. The data is from Birch (1952, 1960, 1961), Bridgman (1949), McQueen *et al.* (1964), Anderson (1964), Verma (1960), Simmons (1964) and Hughes & Maurette (1957). A least squares fit to this data gives

$$\frac{\rho}{\bar{M}} = 0{\cdot}048\,\Phi^{0{\cdot}323} \pm 0{\cdot}12. \tag{37}$$

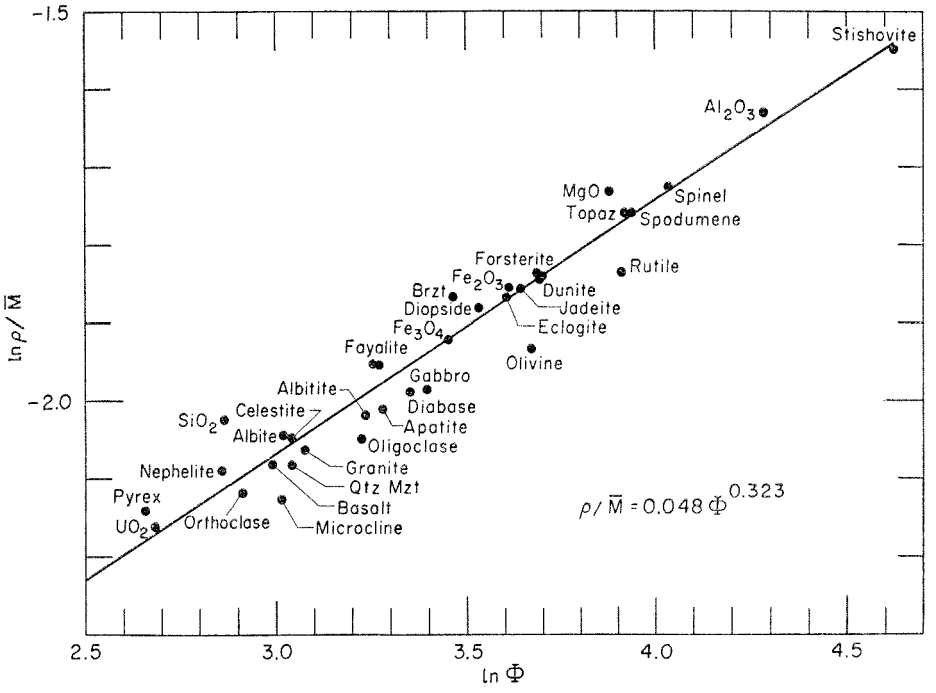

FIG. 2. $\ln \rho/\bar{M}$ vs Φ for selected rocks and oxides; solid line is a least squares fit to this data with parameters as shown.

The standard deviation corresponds to a relative error in density of $\pm 4\%$. In previous notation equation (37) can be written

$$-\partial \ln V = 0{\cdot}323\, \partial \ln \Phi,$$

i.e.

$$-\left(\frac{\partial \ln \Phi}{\partial \ln V}\right)_{T,P} = 3{\cdot}096$$

For comparison, a least squares fit to the precise ultrasonic data of Schreiber & Anderson (1966a, b) on MgO and Al_2O_3 measured as a function of pressure gives

$$\left.\begin{aligned} \frac{\rho}{\bar{M}} &= 0{\cdot}048\, \Phi^{0{\cdot}335} \\ -\left(\frac{\partial \ln \Phi}{\partial \ln V}\right)_T &= 2{\cdot}99 \end{aligned}\right\} \text{(for MgO)}$$

$$\left.\begin{aligned} \frac{\rho}{\bar{M}} &= 0{\cdot}052\, \Phi^{0{\cdot}318} \\ -\left(\frac{\partial \ln \Phi}{\partial \ln V}\right)_T &= 3{\cdot}15. \end{aligned}\right\} \text{(for } Al_2O_3\text{)}$$

The agreement of the parameters which are obtained from compression experiments with those in equations (36) and (37) is remarkable. This lends support to Birch's generalization that, as a first approximation, the velocity in silicates and oxides is determined by two principal variables, density and mean atomic weight.

Table 3

Material	M	Density	Φ
Fe_2O_3	31·94	5·0100	36·390
Fe_3O_4	33·08	4·8660	31·150
Pyrex	19·80	2·3340	14·140
SiO_2	20·03	2·6500	17·360
Stishovite	20·03	4·2800	100·000
Forsterite	20·10	3·1900	39·690
MgO	20·20	3·5803	47·418
Spinel	20·32	3·6300	55·800
Al_2O_3	20·39	4·0000	71·200
Topaz	20·45	3·5350	50·480
Quartz Monzonite (Qtz Mzt)	21·20	2·6490	20·710
Olivine	22·90	3·3240	38·700
Fayalite	29·11	4·1400	26·010
Albitite	20·17	2·6870	25·100
Microcline	21·41	2·5600	20·230
Orthoclase	21·41	2·5800	18·300
Jadeite	20·40	3·1910	37·590
Oligoclase	20·50	2·6500	24·850
Apatite	24·00	3·2180	26·170
Nephelite	21·10	2·6200	17·370
Bronzitite (Brzt)	21·20	3·2830	31·400
Rutile	26·63	4·2600	49·000
Celestite	30·61	3·9600	20·720
Gabbro	21·80	3·0000	29·400
Dunite	20·90	3·3190	39·780
Eclogite	22·20	3·4420	36·230
Diopside	21·65	3·3100	33·700
Albite	20·17	2·6200	20·250
Basalt	20·70	2·5900	19·700
Diabase	22·00	3·0140	28·100
Spodumene	18·80	3·2060	49·500

The value for $(\partial \ln \Phi/\partial \ln V)_T$ may also be compared with the value of -3 which is appropriate for a Birch–Murnaghan solid at zero pressure. Table 4 summarizes least square fits to $\rho/\bar{M} = A\Phi^n$ for other experimental data for oxides. A wide variety of crystal structures and compositions are included. There are systematic deviations which indicate that there are other factors besides the mean atomic weight which contribute to the relation between Φ and ρ but for a first approximation the mean atomic weight provides the main control and $(\partial \ln \Phi/\partial \ln \rho)_{T,P}$ is roughly the same as $(\partial \ln \Phi/\partial P)_T/(\partial \ln \rho/\partial P)_T$. Since $\bar{M}$ is the controlling parameter it appears that the effect of a solid–solid phase change may be very similar to the effect of self-compression alone insofar as the relationship between Φ and ρ is concerned. If true this provides an extremely useful way to integrate through the C-region of the mantle.

Fig. 3 shows the relation between ρ and Φ, with $\bar{M}$ as the parameter from high pressure and shock wave experiments. This data is mainly from McQueen & Marsh (1960) and McQueen (personal communication). Temperature corrections are not

Table 4

A	n	$(\partial \ln \Phi/\partial \ln V)_{T,P}$	
0·056	0·281	3·57	116 Silicates, oxides, titanates and nitrates ($18{\cdot}5<\bar{M}<90$)
0·064	0·240	4·17	29 rocks and oxides ($18{\cdot}5<\bar{M}<90$)
0·059	0·274	3·65	56 rocks and oxides ($18{\cdot}5<\bar{M}<88$)
0·048	0·323	3·096	31 selected oxide minerals and rocks ($18{\cdot}6<\bar{M}<33{\cdot}08$)

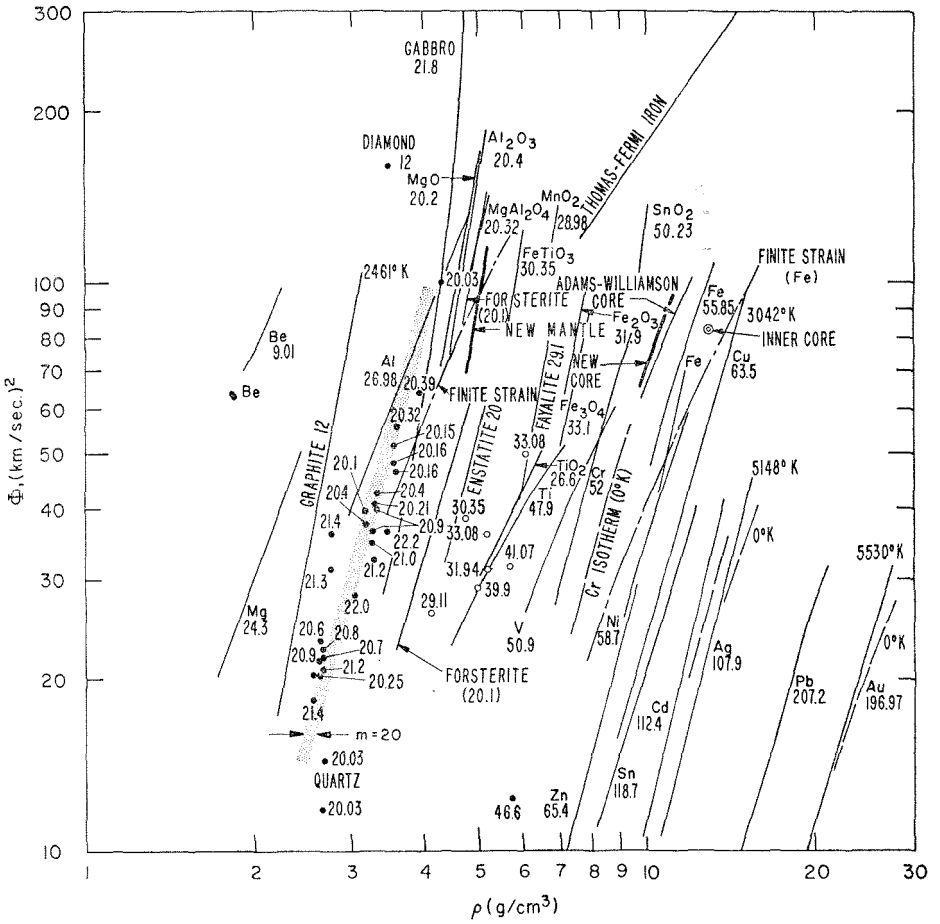

FIG. 3. Density versus Φ as a function of $\bar{M}$ from high pressure and shock wave data. Shock wave data is uncorrected for temperature although the effect of temperature is shown for some elements. Some of the data from Fig. 1 is also shown as isolated points and the stippled band (for $\bar{M}=20$). Data for the Earth and some theoretical curves are also shown.

made except where indicated. Also shown are individual points including some from the previous figures. Most of the data obeys a simple power law although some curvature is evident. A similar plot has been used by Birch (1963) in conjunction with density distributions for the mantle and core to estimate the mean atomic weight in the mantle and core and, in particular, to argue for an iron-rich, rather than a silicate phase-change core.

7. Density distributions for the mantle

An equation of state of the form

$$\rho = A\Phi^n$$

can now be used to convert observed velocities in the mantle to density. An approach similar to that of Birch could be used where the n is assigned for the mantle and core from experimental or other considerations and the A for the mantle and core are then determined by the constraints supplied by the mass and moment of inertia. High pressure and shock wave data can then be used to estimate $\bar{M}$ from A.

The results obtained would not differ greatly from those of Birch if we used the empirical equation (37) since the $\rho-\Phi$ power law and Birch's $\rho-V_P$ linear law both obtain their parameters from least squares fits to similar data. For example, using

$$\frac{\rho_1}{\rho_0}=\left(\frac{\Phi_1}{\Phi_0}\right)^{0\cdot323}$$

from the present work and

$$\rho_1-\rho_0=0\cdot302(V_1-V_0)$$

from Birch (1961) and taking

$$V_0=8\cdot15\,\text{km/s},\ \rho_0=3\cdot59\,\text{g/cm}^3\ \text{and}\ \Phi_0=38\cdot2$$

from Gutenberg's values for the upper mantle, and $V_1=13\cdot7$ and $\Phi_1=118\cdot6$ from Gutenberg's values for the base of the mantle we obtain ρ_1, the density near the base of the mantle to be 5·18 from the power law and 5·27 from the linear law. The Bullen Model A gives 5·66 for this density at the corresponding depth.

Fig. 4 shows the variation of Φ with depth for two sets of seismic data and two density distributions derived from the CIT11A model for different parameters in the power law relationship.

The CIT11A model has two major seismic discontinuities in the upper mantle and the corresponding density models also show these discontinuities. Also shown in this figure are the densities and density jumps associated with the various phase changes that have been proposed for the upper mantle.

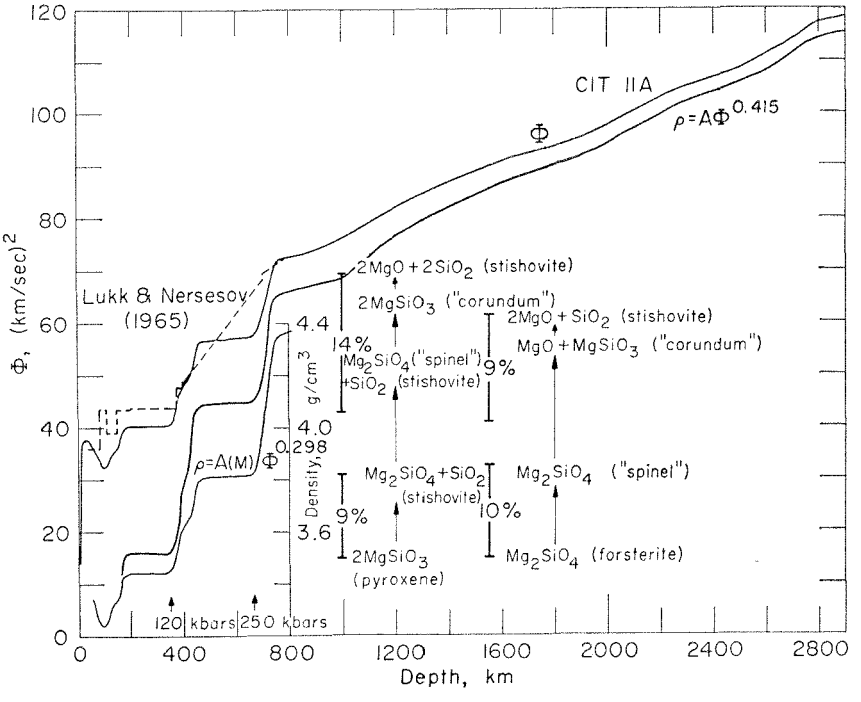

FIG. 4. Φ as a function of depth from data of Anderson & Toksöz (1963) and Lukk & Nersesov (1965). The Gutenberg V_P/V_S ratio is used to find Φ from the V_S model CIT11A. Density is found from Φ with the equations shown and an assigned upper mantle density. The density jumps associated with various proposed phase-changes are also shown. The gaps are estimates of the self-compression between phase changes.

Two possible sequences of events in the transition region of the mantle are (Ringwood & Seabrook 1962, Sclar *et al.* 1964):

A. Pyroxene ($MgSiO_3$)

(1) $2MgSiO_3 \rightarrow Mg_2SiO_4 + SiO_2$ (stishovite)

$\Delta\rho \sim 9\%$

(2) $Mg_2SiO_4 + SiO_2$ (stishovite) $\rightarrow Mg_2SiO_4$ ('spinel') $+ SiO_2$ (stishovite)

$\Delta\rho \sim 7\frac{1}{2}\%$

(3) $Mg_2SiO_4 + SiO_2 \rightarrow 2MgSiO_3$ ('corundum')

$\Delta\rho \sim 4\frac{1}{2}\%$

(4) $2MgSiO_3 \rightarrow 2MgO + 2SiO_2$ (stishovite)

$\Delta\rho \sim 2\%$

B. Olivine (Mg_2SiO_4)

(1) $Mg_2SiO_4 \rightarrow Mg_2SiO_4$ ('spinel')

$\Delta\rho \sim 10\%$

(2) $Mg_2SiO_4 \rightarrow MgO + MgSiO_3$ ('corundum')

$\Delta\rho \sim 8\%$

(3) $MgO + MgSiO_3 \rightarrow 2MgO + SiO_2$ (stishovite)

$\Delta\rho \sim 1\%$

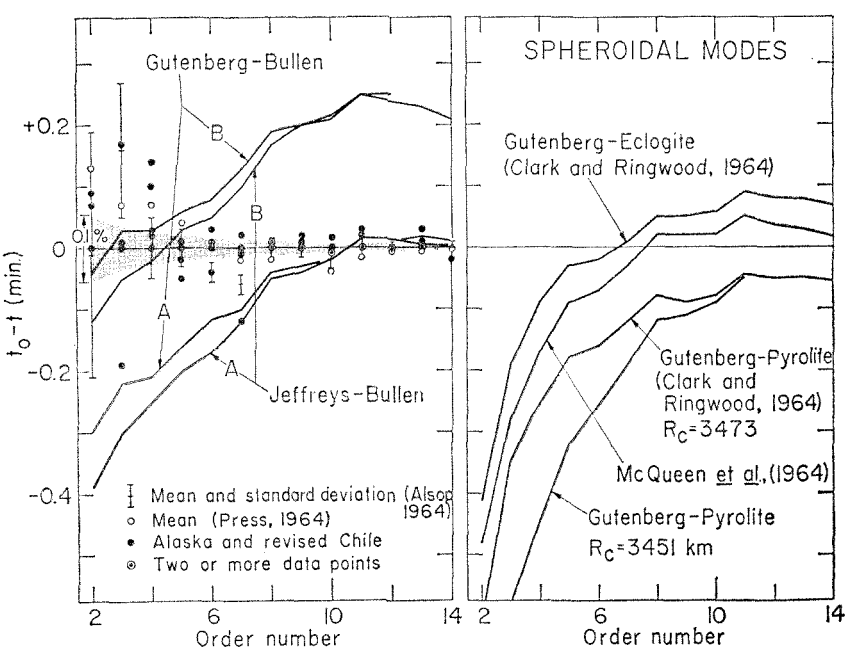

FIG. 5. Difference between 'observed' (t_0) periods of spheroidal free oscillations and calculated (t) periods for various theoretical Earth models as a function of order number for spheroidal modes 2–14. The 'observed' periods have been taken as S_2(53·82), S_3(35·55), S_4(25·75), S_5(19·82), S_6(16·07), S_7(13·54), S_8(11·78), S_9(10·57), S_{10}(9·668), S_{11}(8·934), S_{12}(8·368), S_{13}(7·882) and S_{14}(7·468), all in minutes. Other observations are shown by points and error bars. Results are shown for several values of the core radius, R_c.

These reactions have been predicted to occur between depths of about 450 and 800 km. The total density changes in reaction series A and B are approximately 24% and 20%, respectively. The change in Φ between 400 and 800 km is 55%, giving a density jump of about 18% from the ρ–Φ relation, equation (37). The estimated density jumps for the phase changes are based on zero pressure estimates of the density and are therefore over estimates since the lower pressure phases are more compressible than the high pressure phases.

The use of a single equation of state with constant parameters throughout the mantle is only a first approximation. If only the mass and moment of intertia were known this would be as far as we could go. However, the periods of free oscillation supply new data pertinent to the problem.

Fig. 5 shows the general situation, summarizing both the observations and the theoretical fits of the standard density distributions to the spheroidal oscillations. Of the standard models the Bullen B densities are better for the low order modes and Bullen A is better for the higher order modes. However, as shown in Fig. 5, the general trend of both is wrong.

The procedure we follow, which will be described in detail in a later paper, is to split the Earth into its major subdivisions each of which has its own ρ–Φ equation of state. The parameters are then found by requiring that the mass, moment of inertia and periods of free oscillation be satisfied. In practice, it has been found sufficient to consider only the upper mantle, the entire lower mantle including the *C*-region, the outer core and the inner core; thus only eight parameters need be determined from the data. As the data becomes more complete, particularly for the overtones of the free oscillations, the transition regions in the upper and lower mantles and between the inner and outer cores can be treated separately, but it has been found possible to satisfy the present data with only the eight parameters mentioned above.

8. Summary

The present paper had several purposes. One was to re-emphasize the importance of compression, or volume change, as the important variable in geophysical equations of state and to suppress the importance of pressure. The second was to relate volume, or density, to seismically available information. The third was to consider the effects of temperature, pressure, phase changes and composition on this relationship. A fourth was to indicate a method for carrying the equation of state across the troublesome inhomogeneous *C*-region. And finally, for illustration, density models for the Earth were constructed based on these considerations. The actual motivation for this study was to determine a plausible relationship between seismic velocities and density with a minimum number of parameters which could be found from free oscillation data.

The use of seismic parameters to determine density is, of course, not novel and is the basis of the Adams–Williamson–Bullen method. However, this conventional approach, besides using questionable assumptions, must handle questions of inhomogeneity and temperature outside its own framework and is basically an extrapolation scheme. Our scheme is in the spirit of the Birch velocity–density hypothesis which gives a one-to-one relationship between density and velocity rather than using the local seismic velocities to extrapolate the local density. It differs from the standard equation of state approach in the same way. Rather than using a pressure–density equation of state and the assumption of hydrostaticity to integrate through a homogeneous region we associate a density with a seismic property and can use the parameters relating the two to estimate, for example, the composition of the mantle.

The density in the mantle varies, roughly, from 3·3 to 5·6. The fractional changes in density in the various regions of the mantle are relatively small: 10% in the upper mantle, 20% in the transition (*C*) region, and 20% throughout the remainder of the

lower mantle. Current evidence seems to suggest that the variation of density in the lower mantle is primarily due to the effects of pressure and that temperature, pressure and, possibly, composition and polymorphic transitions all contribute to the variation of density in the upper mantle. The rapid increase of density in the *C*-region is probably controlled mainly by solid–solid phase changes. Compressions ($-\Delta\rho/\rho_0$) of the order of 2 have been obtained in the laboratory on the more compressible elements and this data has been satisfactorily treated by conventional, nominally low-pressure equations of state. Although the pressures at the base of the mantle are of the order of $1{\cdot}4 \times 10^{12}$ dyn/cm^2 the total compression in regions to which we have little hesitation in applying a single equation of state do not make severe demands on present experience with theoretical and experimental equations of state.

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